Review

# Recent advances in the development of Li–air batteries

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HIGHLIGHTS

► The recent state-of-the-art focused on rechargeability is herein reported.
► We describe new catalysts and selective membranes for the cathode protection.
► We discuss the last findings on electrolytes decomposition during cell operation.
► Different electrolytes are described with advantages and limitations.
► Critical issues of the different compartments are addressed.

GRAPHICAL ABSTRACT
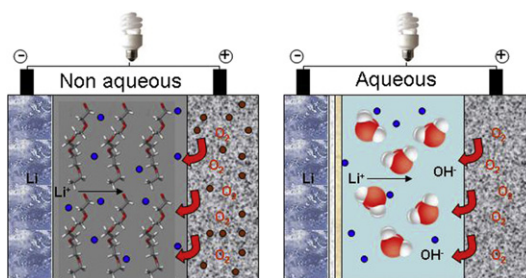
ARTICLE INFO

ABSTRACT

The global energy demand calls for more efficient storage systems. In this review, the state of the art of Li/air and Li/O$_2$ batteries is discussed with particular attention on the more recent findings regarding all the battery compartments. Both aqueous and non-aqueous systems are considered, and the most critical issues for better battery design are addressed. Whereas the predicted charge/discharge values for these devices do justify the intense research efforts performed nowadays, great problems are still present which must be overcome in order to make Li/air and Li/O$_2$ a reality for future large-scale applications.

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1. Introduction

The growing global energy demand of modern society is urging to find large-scale sources, which are more sustainable and environmentally friendly of the oil-based ones. The increase of CO_2 emissions and also the limited availability of oil, call for the search for sources of clean energy. In this context, electrochemical systems for energy production, conversion and storage, including super capacitors, fuel cells and batteries, may play a relevant role. In particular, rechargeable lithium 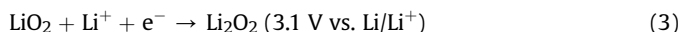batteries are expected to play a key role also in future energy storage, including both stationary (smart grids) [1] and automotive (fully electric or hybrid vehicles) applications [2–4]. At present, the capacity of the state-of-the-art lithium ion battery is limited by the positive electrode, which can store only about 150 mAh g^{-1} of charge compared with about 300 mAh g^{-1} of the graphite anode. The effort to design better electrodes will likely improve the energy density but, at best, by no more than a factor of two. Therefore, radically different approaches are required in order to fulfil the very demanding requests of energy storage. A very interesting approach in this sense is offered by the lithium–air battery (LAB), also called lithium–oxygen (Li/O$_2$), which belongs to the family of the metal/air devices [5]. A typical cell design is constituted by a lithium metal anode, a porous carbon cathode and an electrolyte (comprising a dissolved

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lithium salt). During the discharge the Li metal anode oxidizes to Li^+ and electrons flow through an external circuit, while Li^+ diffuses towards the cathode via the electrochemical potential gradient. O_2 from the atmosphere is reduced at the porous cathode thus forming Li_2O_2 and, at a less extent, Li_2O. Here, the reactants no longer have to be carried on-board, and the supply of O_2 is, in principle, infinite. While the use of an O_2-based cathode can potentially assure specific energy values 5–10 times greater than those of the present batteries, it is difficult to estimate the LABs practical values, which depend on the Li-byproducts formation at the cathode during discharge. Theoretical values of 3505 Wh kg^{-1} and 3582 Wh kg^{-1} have been recently quoted in case of non-aqueous and aqueous electrolytes, based on the reactions $O_2 + 2Li \rightarrow Li_2O_2$ and eq. (8) respectively [2], and taking into account also the mass of Li and of O_2 gained during discharge. These values must be compared with that of methanol/air fuel cell (5524 Wh kg^{-1}), and gasoline/air engine (11,860 Wh kg^{-1}) [6]. These high values make LABs particularly appealing for the automotive applications.

The practical feasibility of a rechargeable LAB with organic electrolyte has been early proven by Abraham and Jiang [7]. The obtained capacity was about 1300 mAh g_C^{-1}, and the cell was cycled several times. The reduction product at the cathode is Li_2O_2, although the formation of Li_2O may be favoured at high discharge rates [8]. The possible cathodic mechanism could involve the following reactions:

$$O_2 + Li^+ + e^- \rightarrow LiO_2 \ (3 \ V \ vs. \ Li/Li^+) \tag{1}$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \tag{2}$$

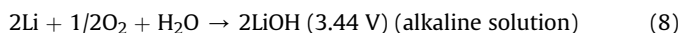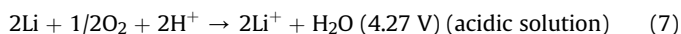$$LiO_2 + Li^+ + e^- \rightarrow Li_2O_2 \ (3.1 \ V \ vs. \ Li/Li^+) \tag{3}$$

which are generally referred as "Oxygen Reduction Reactions" (ORRs) [2]. In addition, some irreversible reactions have been suggested to contribute to the cathode chemistry during the discharge [9]:

$$4Li^+ + O_2 + 4e^- \rightarrow 2Li_2O \ (2.91 \ V) \tag{4}$$

$$Li_2O_2 + 2Li^+ + 2e^- \rightarrow 2Li_2O \ (2.72 \ V) \tag{5}$$
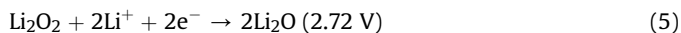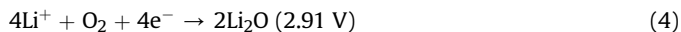
The electrochemical decomposition of Li_2O_2 to Li and O_2 on charging has been later demonstrated by Ogasawara et al. [10] and the corresponding reaction is often referred as "Oxygen Evolution Reaction" (OER):

$$Li_2O_2 \rightarrow 2Li^+ + 2e^- + O_2 \tag{6}$$

Also aqueous electrolytes were proposed [11], and in this case the cell reactions are:

$$2Li + 1/2O_2 + 2H^+ \rightarrow 2Li^+ + H_2O \ (4.27 \ V) \ (acidic \ solution) \tag{7}$$

$$2Li + 1/2O_2 + H_2O \rightarrow 2LiOH \ (3.44 \ V) \ (alkaline \ solution) \tag{8}$$

Schemes of LABs with both non-aqueous and aqueous electrolytes are reported in Fig. 1.

To date the organic cell seems to be preferred, at least for very large-scale and massive applications such as those required by
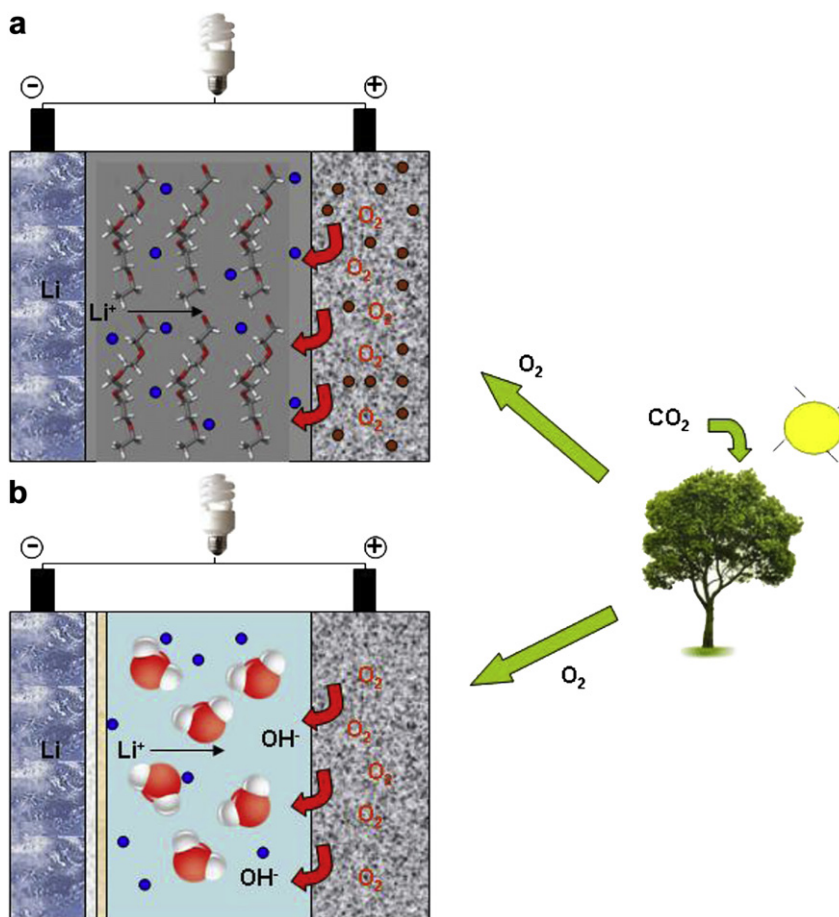

Fig. 1. Schematic representations of a) aprotic and b) aqueous lithium–air batteries.

automotive. In fact, the use of aqueous electrolytes does likely require the same noble metals catalysts employed in polymer fuel cells, which indeed would limit LABs massive applications. Moreover, in case of aqueous electrolyte, an anode-protecting layer with high Li^+ conduction (e.g. a ceramic compound, see Ref. [12]) is required, which makes the cell more complex (see Fig. 1b). Although different cell configurations have been proposed, such as the fully solid state architecture with ceramic electrolytes [13] and the mixed aqueous aprotic system [14], they still need a deep investigation of the reaction mechanisms and the solution of serious structural design problems to deserve industrial development.

Despite of some promising results, however, a real breakthrough has still to be made in this field to make rechargeable Li/air batteries ready to the market. Several serious problems must be solved to assure proper cyclability and therefore rechergeability, including: i) decomposition of the organic electrolyte at the cathode, ii) protection of cathode from CO_2 and H_2O by means of a proper O_2-permeable membrane, iii) lowering of the Li_2O_2 oxidation overpotential on charge. Another key point is to obtain higher current densities from the battery, which can be pursued by improving the electrolyte conductivity, and by lowering the interfacial contact resistance among the compartments. More in detail, each compartment of the LAB presents many critical issues to be addressed. The electrolyte must provide nearly the same level of ionic conductivity mandatory for lithium ion batteries (at least 1 mScm^{-1} at room temperature) and high Li^+ transport number [12]. Moreover, it must be hydrophobic to prevent/reduce moisture reaction with the lithium anode, electrochemically stable at the anode and the cathode (i.e. more than 3.5 V with the present catalysts), chemically stable towards Li_2O_2, Li_2O and O_2^- radical and, finally, able to dissolve O_2 and to allow it to diffuse rapidly at the cathode interface. Here, the starting point of the research has been given by the know-how developed for Li-ion batteries, and the most common organic electrolytes have been screened [8,15,16]. Good performances were obtained with ether-based electrolytes such as 1 M $LiN(SO_2CF_3)_2$ (LiTFSI) in 1:1 1,3-dioxolane:1,2-dimethoxyethane (DOL−DME), which allowed capacities higher than 2000 mAh g^{-1} [15]. However, these liquids are flammable and not hydrophobic. For this last reason, even in this case it is necessary to shield the lithium anode with a protective layer [17]. Ionic liquids (ILs) may be a good choice to overcome these issues.

Concerning the cathode, the overpotential issue on charge is relevant. As a matter of fact, there is a ∼1 V gap between charge and discharge which could be reduced using a proper electrocatalyst [2,18]. However, these studies were performed with electrolytes based on organic carbonates that now we know can undergo decomposition during cycling, and this reaction could contribute to the overpotential. Actually, these problems involving the cathode reactions restrict the rechargeability of the cell and some concerns arise about the real feasibility of the LABs. On the other hand, efforts to find new materials more suitable than those applied in Li-ion batteries are required because the results so far obtained seem to indicate that a direct transfer of the know-how of Li-ion is not sufficient. In addition, if one envisages large scale applications (e.g. in automotive) massive amounts of air are expected to flow into the battery, and even small percentages of moisture could be detrimental. At present, it is not fully clear if catalyst is really necessary for the charge process. If yes, however, its nanostructure is relevant [19], and the investigation of the role of electrocatalytic particles with nanometric dimension is mandatory to increase the cyclability of the battery, and/or to improve the specific capacity stored after each recharging cycle. New nanostructured and/or hierarchically structured materials need to be individuated for the preparation of the positive electrode of a Li/air

battery and several works on this topic have been recently published [20−22].

In this review we will address the most important issues in LABs development. A great deal of attention will be devoted to the main compartments of the battery and to the proposals aimed at solving their critical problems, by referring to both aqueous and non-aqueous systems. In particular, we will focus on new catalysts and selective membranes for the cathode protection and to the development of protecting layers for the anode. Recent findings regarding electrolytes behaviour in cell and the development of new types of electrolytes will be finally discussed.

2. Cathodic compartment

A common feature of all kind of LABs is the air cathode based on carbon. The intrinsic characteristics of carbon, such as porosity, surface area and morphology can affect the performances of the cell, considering that the discharge products in aprotic cells are incorporated in the carbon cathode and wait to be decomposed during the charge. Many works have been devoted to the comprehension of the factors that mainly influence the cycling and it seems that carbon porosity and pore volume represent the key aspects for reducing the charge overpotential and assuring a long cycle life. Mesoporous carbons, both commercially available and synthesised in laboratory, are usually employed and it was reported that the decrease in capacity at high current density can be due to the blockage of the pores by the discharge products, which, in some cases, cannot be removed during the subsequent charge process [23,24]. The reaction mechanisms at the cathode and electrolyte interfaces, and so the diffusion kinetics, are affected by the Li_2O_2 location inside the pores (see Fig. 2) and some studies have been done to find the relationship between the discharge time and the dimension of the pores which host the oxides precipitates [23]. The Li_2O_2 particles not only accumulate in the porous matrix during the discharge, but also block the gas and the electrolyte transfer [24]. Density Functional Theory (DFT) calculations applied to surface area data clearly show that the discharge capacity is closely related to the surface area of pore larger than 20 Å. Fig. 3 shows how the solid Li oxides would be formed and accommodated during the discharge into micro-, meso- and macro-pores; in case of a majority of micropores the mass transfer is blocked and the interface reactions are inhibited. Recent findings lead to the hypothesis that the
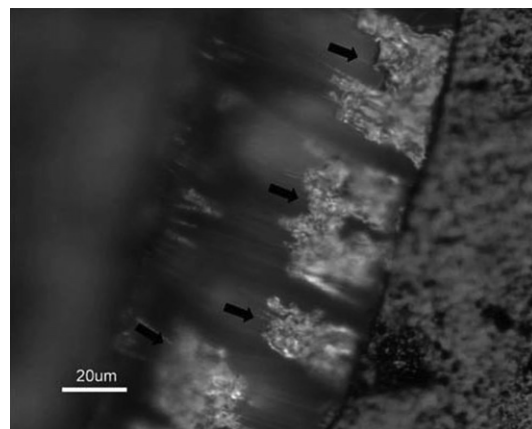

Fig. 2. Optical microscope picture for a cathode made of CuFe catalyzed K-carbon in Li/air cells discharged at 1.0 mA cm^{-2} to 1.5 V, rested for 5 h, and then discharged at 0.05 mA cm^{-2} to a total capacity of 850 mA h g^{-1}. Deposits from cathode reaction of discharging Li/air cells were seen as colourless crystals formed (shown by arrows) within the cracks of the cathode (taken from Ref. [23] with permission from RSC).
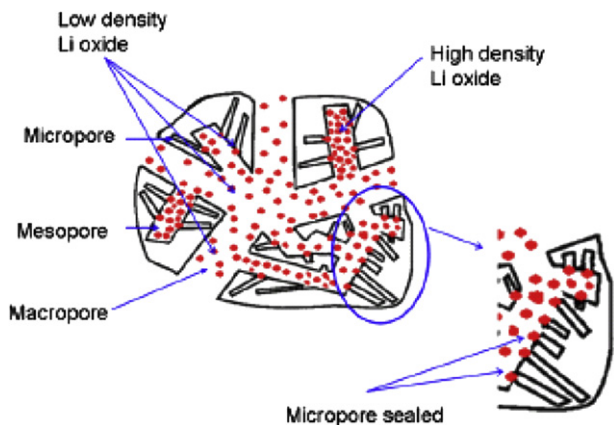
Fig. 3. Accommodation of Li oxides in the pores of various sizes (taken from Ref. [24] with permission from Elsevier).

Table 1
Comparison among the ORR and OER voltages by using different catalysts. The electrolyte used in each case is also reported.

Catalyst	Electrolyte	ORR V vs. Li$^+$	OER V Li$^+$	Ref.
Au	LiClO$_4$ 1 M in PC:DME 1:2	2.7	4.2	[18]
MnO$_x$	LiPF$_6$ 1 M in PC	2.6	4.2	[22]
CuFe	LiOTf 0.2 M in PC:TFP 7:3	2.5	–	[23]
β-MnO$_2$/Pd	1 M LiTFSI in EC:DEC 3:7	2.9	3.6	[37]
Pd	LiPF$_6$ 1 M in PC	2.6	3.9	[39]
Pt		2.7	4.0	
Ru		2.75	3.95	
MoN/NGS	LiPF$_6$ 1 M in EC:DMC 1:1	3.1	4.0	[44]
Li$_5$FeO$_4$	LiPF$_6$ 1 M in PC	2.7	4.1	[48]
Li$_2$MnO$_3$·LiFeO$_2$		2.8	4.0	
Fe$_3$O$_4$	LiPF$_6$ 1 M in PC	2.6	4.1	[41]
CoFe$_2$O$_4$		2.6	4.3	

large reduction in the discharge voltage and capacity with increasing current rates can be attributed to the resistance associated with solid-state Li$^+$ diffusion in the lithium peroxide during discharge [25]. Due to the important role of the cathode microstructure, different carbon morphologies have been studied and proposed to be used in LABs. For example, mesocellular carbon foam seems very promising to reach good capacity due to an appropriate particle size and ultra-large mesopores structure [26]. Highly mesoporous nitrogen-doped carbon [27,28] and carbon nanotubes cathode [29] showed better performances in comparison with undoped analogue, due to both an increased electrocatalytic activity and to a high porosity that favours O$_2$ diffusion. Other authors [30] demonstrated a good cell response using a carbon nanofiber electrode grown directly on porous substrate. The oxygen pressure plays also an important role in the capacity of the LABs and some papers report that p_{O_2} has to be sufficient to prevent a deep electrolyte penetration in the porous carbon without inhibiting the mass transport ensured by the electrolyte itself [24]. Generally speaking, an increase of the oxygen pressure leads to higher discharge times due to the increased solubility of O$_2$, especially for pressures of 10–11 atm [31]. Considering the high importance of the O$_2$ diffusion, some attempts have been made to increase it by adding perfluorinated additives to non-aqueous electrolytes thus substantially increasing the discharge rate capability [32]. Graphene nanosheets (GNSs) have attracted great attention for energy storage applications due to their peculiar morphology and structure which consists of microporous channels facilitating rapid O$_2$ diffusion. Very high capacities have been obtained using GNSs as air cathode thanks also to the numerous active sites disposable for the Li–O$_2$ reactions [33–35].

Several authors have proposed the use of catalysts to favour both ORR and OER and reduce the overpotential between them, so favouring the round-trip efficiency of the cell, but the real role of catalyst during the cycling of the battery is still not clear. In Table 1 ORR and OER voltages for some of the catalysts which will be discussed in the following are reported. The electrolytes used in the different cells are indicated, and for more details on the cathode components and experimental conditions the reader should refer to the specific article. Among the proposed catalysts, many are already applied in fuel cells, in solar cells and in metal air batteries and their catalytic activity is well known. The most used for non-aqueous batteries are: i) MnO$_x$ and MnO$_2$ in different structural forms (α, β, γ) [36–38] because of its low cost and low toxicity, ii) noble metals (Pd, Pt, Au, Ru) and their oxides [18,39], iii) combinations of MnO$_2$ and metals [40], and iv) simple binary oxides of Fe,

Co, Ni and Cu, as well as ternary oxides combining two binary oxides [21,22,41,42]. All of these materials show a good structural stability that represents an advantage for a long term cycling. It has been proved that the catalytic activity of the manganese oxide is effective for particles in the nanometer range and for these reasons the preferred synthesis routes are wet methods, such as *in situ* precipitation [36], redox reactions [22] and sol–gel type reactions using mesoporous templates [37]. In addition, some works discussed the opportunity to prepare carbon supported MnO$_2$ nanocatalysts to improve the electrical connection among the catalysts and the current collector [22,43]. A large surface contact area between the carbon support and the catalyst assures a good electrocatalytic activity and in this way good performances can be achieved [22]. Concerning metal catalysts, detailed studies were performed in order to ascertain their influence on the onset potential of OER and ORR and also to compare the different metals activity during the cycling. As an example, in Fig. 4 the charge discharge profiles of some common metals and metal oxides are compared to that of MnO$_2$ carbon supported cathodes [39]. Transition metal macrocyclic complex catalysts as for example Co-phthalocyanine [7] were also tested, obtaining in this latter case a higher cell discharge voltage with respect to the non-catalyzed carbon, depending also on the cathode pores volume.
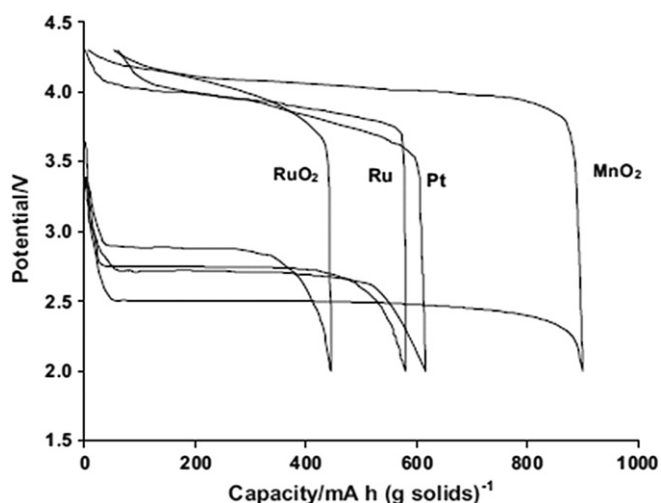

Fig. 4. Voltage–capacity curves on discharge–charge for the Li–air battery with carbon-supported Pt, Ru, RuO$_2$ and MnO$_2$ composite electrodes. This is the first cycle, performed at a rate of 70 mA g$_c^{-1}$ between 2.0 and 4.3 V (taken from Ref. [39] with permission from Elsevier).

The electrocatalytic activity of innovative materials has been recently investigated, achieving encouraging results. Some of these new materials are based on graphene nanosheets [43,44] or carbon nanotubes [45−47], that assure high electronic conductivity, on which nanoparticles of oxides or nitrides have been grown [44]. For example, Dong et al. [44] synthesised a hybrid material of molybdenum nitride nitrogen-doped graphene nanosheets which showed round trip efficiencies comparable to those reported for Pt/Au/C cathode, but with a discharge potential higher than previously reported MnO_2 and Pt/Au/C based cathodes. Other new types of catalysts are lithium metal oxides with a high Li_2O content that should be activated chemically or electrochemically [48]. In this last work, the authors tested Li_5FeO_4 and $Li_2MnO_3 \cdot LiFeO_2$ achieving high capacity, but the round trip efficiency has to be improved due to the low structural stability of these materials. Although the catalyst is largely employed and Debart et al. had shown that Co_3O_4 could lower the overpotential and offer a good compromise between initial capacity and capacity retention [41], the mechanism of its functioning is not completely understood [10].

Catalysts are currently employed also in aqueous systems. Once again, manganese based oxides such as Mn_3O_4 or a composite of MnO_2 and La_2O_3 (or $MnSO_4$ and La_2O_3) have been proposed in the porous electrode for a cell based on alkaline electrolyte [14,49]. Materials such as TiN and N-doped graphene nanosheets have shown considerable catalytic activity for the air-electrode in acidic media [50,51].

Numerous doubts are recently emerging on the real efficacy of the catalyst and, in some cases, it has been shown that electrocatalysis may be unnecessary or even detrimental in aprotic cells [52]. In a very recent publication a complete study of the superoxide radicals reactions with all the possible components of a cell has been carried out (see Fig. 5) [53]. The results clearly show that the high nucleophilicity of the O_2^- radical leads to the formation of other products than Li_2O_2 and in addition, does damage mainly the binder but also the electrolyte, thus changing the subsequent charge mechanism and limiting the rechargeability of the cell. This effect depends on the battery components, in particular on the use and type of the binder for the preparation of the air electrode and also on the organic electrolyte. Other authors recently studied the electrolyte decomposition products, by using spectroscopic techniques [54], and they concluded that the apparently beneficial effects on OER have to be attributed not to the catalyst but to the

electrolyte decomposition. In particular they studied the behaviour of a cell containing 1.2 M $LiPF_6$ in 1:1 wt% ethylene carbonate/dimethyl carbonate (EC/DMC) as electrolyte. In this case the catalyst seems to act directly on the electrolyte decomposition instead of favouring the charge process [54]. These evidences are also supported by previous good results obtained by using a carbon-based cathode without catalysts [23]. In addition, a recent paper reported about the oxygen reduction chemistry in ether- and carbonate-based electrolytes [55] showing that the mixture of EC and DEC (diethyl carbonate) is easily decomposed to Li_2CO_3 and $ROCO_2Li$ (R = alkyl) and corresponding alcohol, compared to DME-based electrolyte. However, also this last decomposes giving H_2O and CO_2 after prolonged exposure to O_2. The successive reaction among H_2O, CO_2 and Li_2O_2 forms again Li_2CO_3.

3. Anodic compartment and electrodes protection

A critical issue for the long-term operation of LABs is the Li-metal anode stability, mainly in view of the practical application in ambient atmosphere, which is well different from the laboratory tests so far performed using mostly pure oxygen, with some exceptions (see for example refs. [56−58]). In fact, metallic lithium easily reacts with moisture and CO_2 present in the air and/or in the electrolyte as contaminants. Aqueous systems suffer in great part of this problem and some approaches are proposed to overcome this limitation that can strongly shorten the battery life. The development of a water-stable lithium electrode has been proposed by several authors [49]. In particular, Visco et al. of Polyplus Battery Company patented a three-layer lithium anode stable in aqueous media (both acidic and basic) [59]. In general, this kind of protection adopts a water-stable Nasicon-type lithium conducting solid glass electrolyte, and in addition, a second protection is inserted between them to prevent undesirable reaction between lithium and this conductive layer. This second layer (buffer layer) has to possess high ionic conductivity and must be stable in contact with Li. At present, different materials are under study such as LiPON [60], Li_3N [61], Cu_3N [59] but also polymer electrolytes can be employed to this purpose. For example, polyethylene oxide (PEO) doped with LiTFSI has been recently tested [61,62] in a Li/PEO_{18}-LiTFSi/LTAP(ceramic electrolyte)/1 M LiCl/Pt cell to study the interfacial resistance evolution and charge discharge cycling. The use of a polymer has been suggested by some authors as a way to prevent the dendrite formation [61], a well known problem when an organic electrolyte is used, which appears after many charge−discharge cycles. A strategy to improve the conductivity of this polymeric layer is the addition of nanosized inorganic fillers such as $BaTiO_3$, SiO_2 and Al_2O_3 [61] or, alternatively, the use of ionic liquids such as N-methyl-N propyl-piperidinium TFSI [62]. A different approach, in which this layer is an organic liquid electrolyte, leads to the development of the so called "hybrid" lithium−air battery [14,63]. In this system, the aqueous compartment is still present and so a protective solid ceramic layer is required as a barrier against water and CO_2. Regarding these solid ceramic electrolytes, the present research is principally focused on materials such as $Li_{1+x+y}Ti_{2-x}Al_xP_{3-y}Si_yO_{12}$ (LTAP), which presents ionic conductivity of the order of 10^{-4} to 10^{-3} Scm^{-1} depending on the preparation method and on the layer thickness [64−66]. Many versions of this material have been investigated looking at an optimal composition able to assure high conductivity and low interfacial resistances [66]. In fact, Wang and Zhou [63] reported that by increasing the current density the operating voltage of the cell abruptly decreases (Fig. 6a) because of the higher resistance of LISICON. The impedance spectrum clearly shows three different semicircles (Fig. 6b) due to the interface resistance (high frequency), charge transfer (medium one) and O_2 diffusion
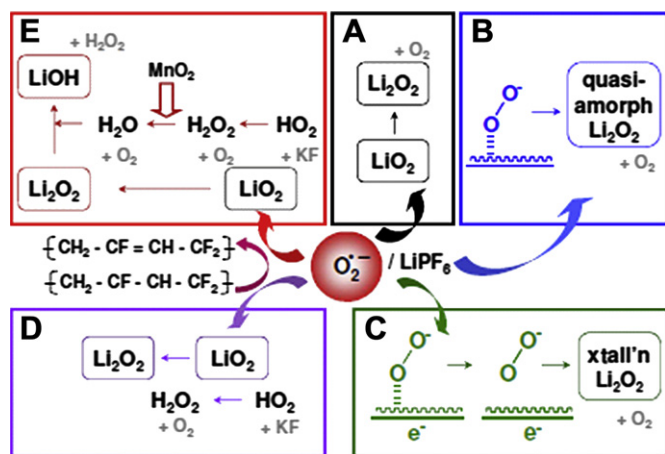

Fig. 5. Exploratory reactions of superoxide that parallel those in a Li−O_2 cell. A) KO_2 + $LiPF_6$/TEGDME; B) KO_2 + $LiPF_6$/TEGDME + carbon; C) electrochemical cell (carbon catalyst); D) KO_2 + $LiPF_6$/TEGDME/PVdF; E) KO_2 + $LiPF_6$/TEGDME/PVdF/α-MnO_2 catalyst. KO_2 = KO_2 (crown ether) (taken from Ref. [53] with permission from ACS).
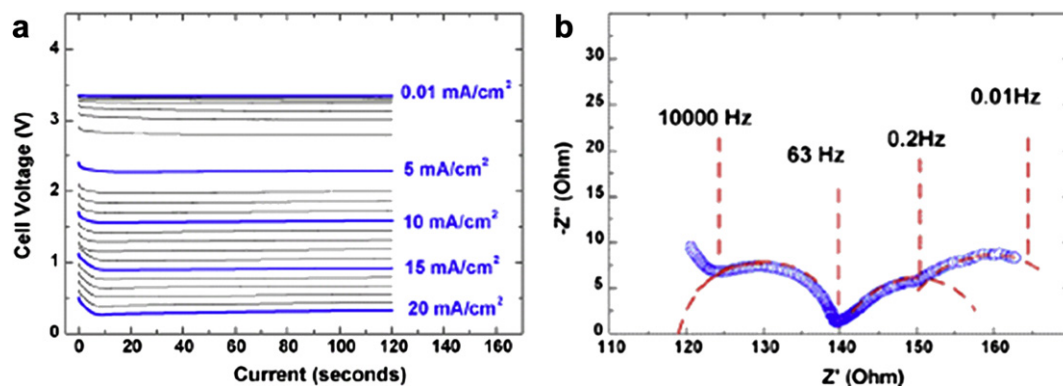
Fig. 6. a) Discharge curves at different current densities and b) impedance spectra at a discharge state of 3 V (taken from Ref. [63] with permission from Elsevier).

resistances (low frequency). Higher current densities make the interfacial resistance to prevail, so causing a voltage decrease. Other interesting compounds alternative to LISICON belong to the garnet and perovskites families [67,68]. The difficulty in developing a protected anode is not only related with the choice of the proper materials, but also with the preparation methods of the thin multi-layers and their contacts. Several deposition techniques can be used to this aim, such as chemical vapour deposition, r.f. and d.c. sputtering, and e-beam evaporation, but their large-scale application remains a challenge because of cost issues. Another critical point is the behaviour of these multiple layers during the stripping and plating of lithium. An *in situ* study of the lithium metal deposition at the LIPON–LISICON interface during cycling [56] demonstrated a decrease of the interface layer uniformity and also its deformation and rupture due to mechanical constraints (Fig. 7).

Different cell designs have been developed in order to prevent the LISICON corrosion in basic solution and to avoid the increase of interfacial resistance. He et al. [69] proposed a Li/air fuel cell with a products recycle compartment to remove LiOH produced by the cell reaction, so protecting LISICON from high pH. The results were promising and the system was discharged for a week reaching good electrode capacity (19,000 mAh g^{-1} based on the total mass of the catalytic layer). An original approach, which avoids the use of aqueous solutions, is based on a cell configuration in which the air electrode is drawn by a pencil directly on the LISICON layer [57] (Fig. 8). The advantages of this system are the absence of the

water and the use of the ceramic electrolyte which can prevent the contact between the organic electrolyte (used on lithium) and the air electrode, thus protecting it from decomposition reactions involving the organic electrolyte during the battery cycling. Another strategy to protect the air electrode from moisture and electrolyte decomposition products has been described by Crowther et al. [70]. These authors developed a cathode protected with a silicone rubber O$_2$-selective membrane, which precludes the water transport from the atmosphere into the lithium air cell and the solvent loss from the cell into the atmosphere. A similar approach for the air cathode protection in aqueous electrolytes has been proposed, which makes use of an anionic polymer electrolyte membrane integrated in the cathode, extending the battery life from a few hours to about 1000 h [56].

4. Electrolyte compartment

During the last years, most of the work carried out on LABs has regarded the development of novel catalysts and cathode materials. In contrast, less advances have been obtained for what concerns the electrolyte, which represents the actual challenge in the optimization of these devices [2,71–73]. In addition to basic properties such as viscosity and ionic conductivity, other important parameters must be considered. As outlined above, the LAB capacity depends on the ability of the electrolyte itself to transport oxygen towards the air cathode. For this reason, the polarity as well as the
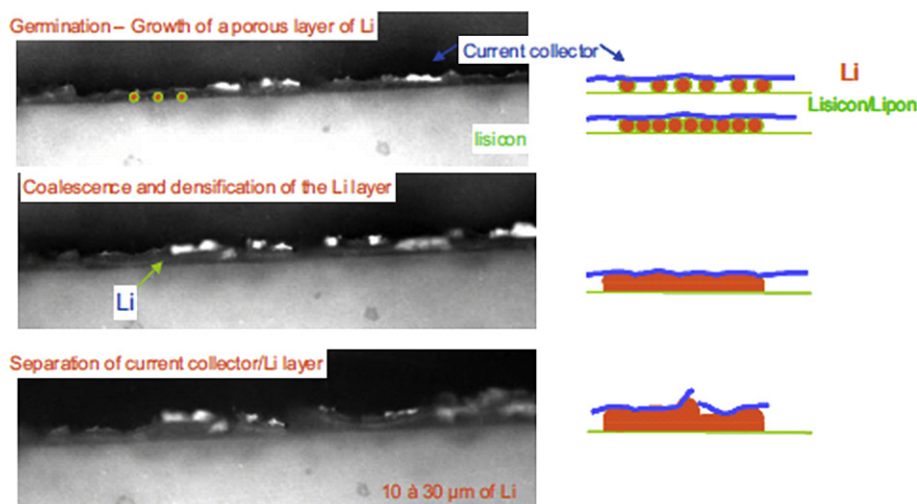

Fig. 7. Optical microscope photographs of Li deposition in an *in-situ* cell, LISICON interface (taken from Ref. [56] with permission from ECS).
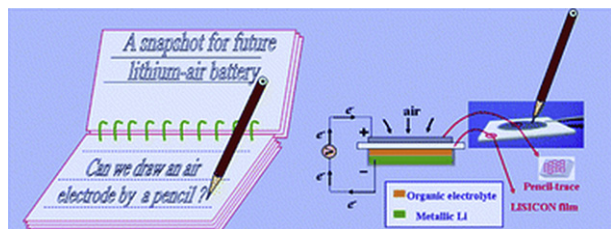
Fig. 8. A schematic representation of the pencil-drawing process and the structure of the proposed lithium–air battery (taken from Ref. [57] with permission from RSC).

O_2 solubility and diffusion are particularly important properties, which must be considered and optimized to guarantee proper gas diffusion through the open pores and to enhance the cell performances [2,71]. The quantity of liquid in the cell also influences the LAB performance by playing a role in the filling process of the carbon porous network, and then on the cell discharge. Xu et al. observed a well-defined maximum of the discharge capacity as a function of the electrolyte amount present in the cell. In particular, specific capacity higher than 160 mAh g_C^{-1} was reached in a coin cell with about 125 mL of 1.0 M LiTFSI in propylene carbonate (PC)–EC (1:1 by wt) [74].

Basically, as anticipated in the previous paragraphs, both Li/O_2 and Li/air batteries may be based on two types of electrolytes, namely non-aqueous and aqueous ones. Although in both cases the discharge process involves the oxygen reduction, the aqueous and non-aqueous systems show different electrochemical behaviours with respect to the cathode [2]. In the non-aqueous cells, the oxygen reduction products are insoluble in the electrolyte, but they form a deposit onto the carbon surface, which fills the available pores and blocks the O_2 access to the reaction sites and its diffusion through the carbon network. For this reason, the actual specific capacity of the Li/O_2 batteries does not correspond to the theoretical one, even though different experimental values are reported using different normalization procedures (e.g. by considering only the carbon weight, the total electrode weight, or even the electrolyte one) [71]. Moreover, the theoretical maximum energy density is estimated on the anode electrode only, but the practical discharge capacity is cathode-limited. Fig. 9 shows two models of reaction zones, recently proposed by Zhang and Foster, which well depict the catalytic reduction of oxygen in both aqueous and non aqueous configurations [75]. The aqueous cells are described by a "three-phase reaction zone" (part a), namely liquid (electrolyte), solid (catalyst/carbon) and gas phase (O_2). In this case the air electrode is dry. In presence of non-aqueous electrolyte, the reduction process may be represented by a two-phase reaction zone model (part b), which means the coexistence of the liquid electrolyte and solid carbon/catalyst. Here, the electrode is wetted
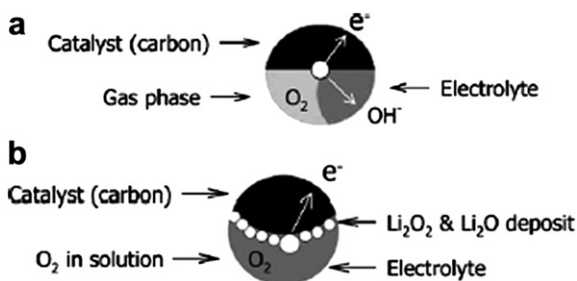
with the solution, and only the oxygen dissolved in the liquid electrolyte may be involved in the charge transfer process occurring at the electrolyte/electrode − and at a some extent at the liquid/oxide − interface.

In conclusions, both advantages and disadvantages of aqueous and non-aqueous electrolytes may be outlined [73]. The aqueous systems lead to the formation of soluble products, so avoiding cathode clogging and volume expansion but the presence of water requires a protective layer on the Li anode, so making more complex the cell fabrication. On the other hand, non-aqueous systems can show specific capacity higher than the aqueous cells, and a better rechargeability [76]. For both cell designs, catalysts based on precious metals could be required. In the following, the state of the art on both non-aqueous and aqueous electrolytes will be reported.

4.1. Non-aqueous electrolytes

After the first report on non-aqueous electrolytes for LABs [7], a lot of cell designs have been described in literature [see for instance Ref. [2] and references therein], which may be based on three different classes: i) organic liquid carbonates and organic solvents, ii) hydrophobic ionic liquids, and iii) polymer (gel) electrolytes.

The organic carbonate-based electrolytes are well proved systems in case of the conventional Li-ion batteries. Their advantages are known, and namely low volatility, good Li compatibility, high ionic conductivity and oxidation stability with respect to the Li/Li^+ couple. In case of Li/air and Li/O_2 cells, several Li salt/organic carbonates combinations were tested, generally based on propylene carbonate (PC) and different co-solvents, such as ethylene carbonate, ethers or glymes, in order to control the oxygen solubility, the solution viscosity and ionic conductivity, the evaporation rate and, above all, the polarity [16,77]. A pioneering work by Abraham et al. about the use of glyme-based solvent for the preparation of gel polymer electrolytes demonstrated their feasibility in Li/O_2 batteries [78]. In addition, $LiPF_6$ dissolved in $CH_3OCH_2CH_2O_4CH_3$ (TEGDME) was tested as the electrolyte with a carbon cathode without catalyst; charge/discharge products, rechargeability of the cell and factors affecting the cycle life were studied without the uncertainties associated with solvent evaporation [79]. Xu et al. carried out a systematic work by testing several Li salts and different solvent mixtures in order to address the effect of salt and solvent compositions on the cell performances. These authors found that both discharge capacity and energy density depend on the nature of the salt. In particular, they found that the systems with LiTFSI show higher O_2 solubility, lower viscosity and higher contact angle than $LiPF_6$ and $LiClO_4$-based electrolytes. Further, although ethers and glymes show higher accessibility to the carbon porous structure, and consequently higher wettability, the carbonate-based cells can provide better cell performances. In particular, they observed that the most performing electrolyte for LABs operating at ambient temperature is 1.0 M LiTFSI–PC/EC (1:1 wt), which delivered a discharge specific capacity of 167.5 mAh g_C^{-1} [16].

In spite of these results, organic carbonates are not good candidates as electrolytes for Li/air and Li/O_2 batteries. Recently, some detailed spectroscopic studies (FTIR, Raman, differential electrochemical mass spectrometry, *in situ* GC/MS) revealed that the organic carbonates undergo decomposition on discharge, rather than to form Li_2O_2 [80–82]. They are, in fact, attacked through nucleophilic reactions by the superoxide species, and a degradation occurs to give H_2O, CO_2, Li_2CO_3, as well as other lithium alkylcarbonates, such as HCO_2Li, CH_3CO_2Li, $C_3H_6(OCO_2Li)_2$, at the cathode. The charging process involves the oxidation of the

Fig. 9. Models of the reaction zones for catalytic ORR. (a) aqueous electrolyte-based cells: "three phase reaction zone"; (b) non-aqueous electrolyte-based cell: "two-phase reaction zone" (taken from Ref. [75] with permission from Elsevier).
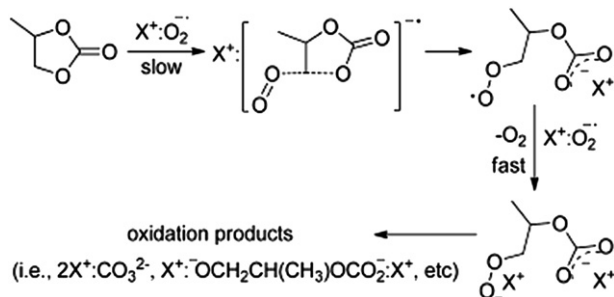
Fig. 10. Decomposition process of propylene carbonate in presence of superoxide-species (taken from Ref. [83] with permission from ACS).
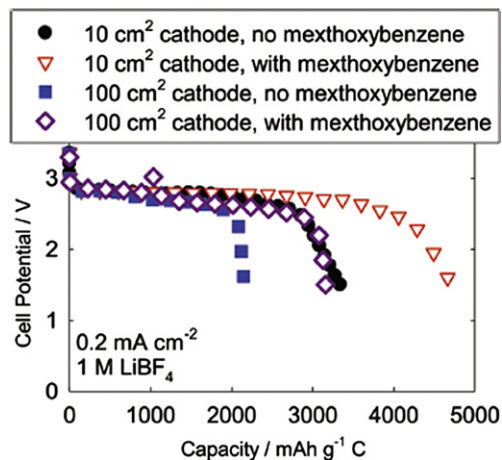

Fig. 12. Voltage profile at a constant current density discharge (0.2 mA cm^{-2}) in oxygen atmosphere of differently sized-cells, using 1.0 M LiBF$_4$ in PC:DMC as electrolyte, with and without methoxybenzene (taken from Ref. [86] with permission from ECS).

carbonates with evolution of water and CO$_2$. A possible reaction scheme is reported in Fig. 10. Several mechanisms were highlighted even by means of computational studies [83].

Therefore, the reversibility of the Li/O$_2$ chemistry is only apparent, because the oxide and peroxides are produced by a subsequent oxidation of the alkylcarbonates. Freunberger et al. performed spectroscopic studies correlated to the electrochemical investigations on Li/O$_2$ cells with alkyl carbonate electrolytes [82]. They showed how the decomposition products tend to accumulate at the cathode surface, and that a failure mechanism occurs which involves the electrolyte consumption with consequent effects on the cell cycling behaviour (fast capacity fading). Fig. 11 reports the FTIR spectra (part a) and the cycling behaviour of a composite cathode cycled between 2 and 2.4 V in a Li/O$_2$ cell with 1.0 M LiPF$_6$ in PC as electrolyte (part b). From the analysis of the plots, it is possible to state the predominant formation of Li$_2$CO$_3$ and an increasing accumulation of both lithium formate and lithium acetate in correlation to a significant capacity fading [82].

To improve the cell performances in presence of carbonate-based electrolytes, the use of additives or co-solvents in PC, EC or DMC solutions has been proposed. Zhang et al., for instance, observed some improvements in the discharge profile of cells based on Li−triflate−PC/DME or Li−triflate−PC electrolytes, by adding fluorinated solvents such as MFE, trifluoroethylphosphates (TFP) or phosphites (TTFP) [84,85]. In particular, they proved that these improvements are more significant at higher discharge current densities, following the order PC/TFP > PC/TTFP > PC. In the authors' opinion, this phenomenon is compatible with an increase of the oxygen solubility when the fluorinated co-solvents are

blended with the electrolyte. However, negative effects of such additives are a higher viscosity of the solvent blend which leads to a lower ionic conductivity of the electrolyte. Co-solvents and additives are also able to improve the partial dissolution of the discharge products, Li$_2$O$_2$ and Li$_2$O, in solvents like PC and DMC. The result is a higher cell discharge capacity. These effects were observed by Xu et al. in presence of a proper amount of tris(-pentafluorophenyl)borane in LiTFSI/PC-EC solutions [74]. Similarly, Crowther et al. found that, in presence of some amount of methoxybenzene in the LiBF$_4$−PC/DMC electrolyte, the discharge capacity of the Li/air cell exceeded 3000 mAh g$_C^{-1}$, which means an increase of 46.6% compared to the system discharged with the methoxybenzene-free solution [86]. The relative voltage profiles of the discharge step are reported in Fig. 12. The positive effects of methoxybenzene are also observed in case of larger cells, although in this case the capacities are lower due to a lower electrolyte uptake and a greater carbon loading.

Finally, a promising choice seems to be given by a novel family of boron esters (Y−C((CH$_2$O)(Z$_1$O)(Z$_2$O))B (where Y = CH$_3$, NO$_2$ and Z$_{1,2}$ = CH$_2$, CO)), whose Lewis acidity may favour the partial or full dissolution of Li$_2$O$_2$ and Li$_2$O in solvents like EC/DMC and DMF [87]. Quaternary ammonium-based salts were also used to improve the
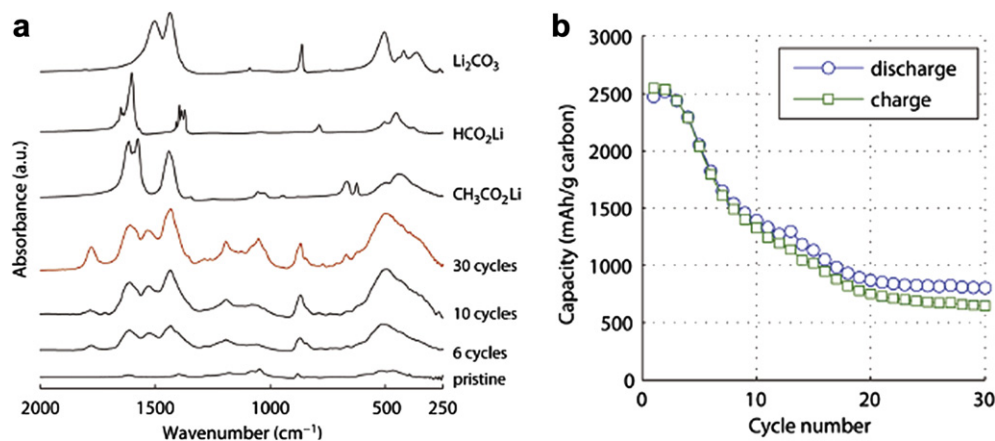

Fig. 11. (a) FTIR spectra of composite electrodes and (b) discharge and charge capacity vs. cycle number for a composite electrode cycled between 2 and 4.2 V in 1 M LiPF$_6$ in PC under O$_2$. Spectra of Li acetate, formate, and carbonate are shown for comparison (taken from Ref. [82] with permission from ACS).

discharge performances of Li/O$_2$ cells. In particular, the addition of 5 mol% of NBu$_4$SO$_3$CF$_3$ into PC or PC/DME-based electrolytes increased the cell discharge capacity from 723 mAh g$_C^{-1}$ to 1068 mAh g$_C^{-1}$. This effect can be due to the phase transfer catalyst properties of the quaternary ammonium in the reduction reaction of Li$_2$O$_2$ into Li$_2$O [88]. Recently, even crown ethers were tested as additives in the carbonate-based systems. Depending on the type of macromolecules, they are able to improve the solubility of the discharge products in the carbonate electrolytes. It was observed that the use of 15 wt% of 12-crown-4 increased the discharge capacity of the Li/air cell of 28% with respect to the control electrolyte [89].

In order to overcome the chemical instability problems of the organic carbonates, other organic solvents were tested to evaluate their effects on the ORR [90,91]. Several types of both linear and cyclic ether-based electrolytes have been, for instance, been investigated, and namely dimethoxyethane, dioxolane and methyltetrahydrofurane [9,92]. By combining electrochemical and structural analyses, it was shown that in the first discharge cycle the decomposition products are accompanied by Li$_2$O$_2$. However, the amount of this product decreases on cycling in favour of the undesirable electrolyte decomposition. For these reasons, even the ether-based electrolytes might not be good candidates in case of both Li/air and Li/O$_2$ cells.

Interesting potential applications as electrolytes for non-aqueous LABs are, in contrast, observed in the case of poly-siloxanes systems. Recently, computational and experimental studies compared the decomposition reactions of siloxanes in their oxidised state with those of their carbon analogues, proving a better chemical stability against the oxygen reduction due to the presence of Si–O groups [93,94].

Hydrophobic ionic liquids (ILs) were also tested for applications in LABs. However, few details are still available, although they have been largely employed in case of the conventional Li-ion cells [12]. The ILs hydrophobicity is indeed of advantage for LABs, since it reduces the compatibility problems with the Li anode. Comparative studies on several imidazolinium-based ionic liquids, performed at 20 °C and high humidity (90%), have shown that water contents less than 1% after 100 h of moisture exposition may be observed in case of 1-ethyl-3-methyl-imidazolinium bis(trifluoromethanesulfonimide) (EMITFSI). This compound also guarantees a discharge capacity higher than 5300 mAh g^{-1} and prevents electrolyte vaporization and hydrolysis of the anode [95]. Fig. 13 reports the voltage profiles on discharging of Li/air cells based on some ILs. Further, the Li/air cell, using EMITFSI, was discharged for 56 days at low current rate of 0.01 mA cm^{-2} in air at 60% RH [95]. More recently, the effects of the ionic liquids on the ORR were evaluated on cells based also on pyrrolidinium (PYR$_{14}$-TFSI), etherpyrrolidinium (PYR1$_{2O1}$-FAP), and EMITFSI systems [96]. In every case, the presence of the lithium salt affects

the O$_2$ reduction and evolution. In the particular case of EMITFSI, cyclic voltammetry measurements revealed highly rechargeable ORR, obtaining Li$_2$O and Li$_2$O$_2$, which underwent several cycles without electrode passivation [97].

The ionic liquids were also used as components in poly-(vinylidene fluoride) (PVDF) based gel electrolytes. A propylimidazolinium–TFSI–silica–PVDF/HFP gel was recently prepared and tested as electrolyte for LABs [98]. Discharge capacity of 2800 mAh g$_C^{-1}$ was delivered, which is higher than that obtained in case of pure ionic liquid system (1500 mAh g$_C^{-1}$). This improvement has been interpreted by invoking a more stabilised interface in consequence of the polymer presence, which acts as a protecting layer of the Li anode against moisture. Although ILs are in principle very attractive as liquid electrolytes and are under testing in many industrial and academic laboratories, the route to their implementation is still long, even for lithium ion batteries. Many basic aspects are yet to be clarified, in particular as far as concerns the stability of the interface with the electrodes.

The demonstrated unsuitability of the organic carbonates and many other solvents for Li/air and Li/O$_2$ batteries is moving the research interest towards the all-solid-state Li/air cells, which show some potential advantage in terms of increased interfacial stability, safety and longer cycle life, due to the protecting role of the solid electrolyte. Some possible configurations have been proposed, ranging from polymer systems to less conventional laminated glass ceramic/polymer ceramic ones [99–101]. Hassoun et al. recently presented the investigation of O$_2$ electrochemistry in a Li/air cell with a PEO-based composite electrolyte. The authors observed that both the electrodes and the electrolyte display an excellent condition after the cycling test. Further, CV runs performed at low currents showed a perfect deconvolution of two peaks relative to the electrochemical formation of Li$_2$O$_2$ and Li$_2$O [101].

4.2. Aqueous electrolytes

Differently from the non-aqueous electrolytes, for which numerous kinds of liquid or solid ionic conductors are under study, the aqueous ones are limited to weak or strong acidic or basic solutions. As already stated before, the main advantage of aqueous LABs is that the water is not a limiting factor of the cell performances. Further, the discharge products are generally soluble in the aqueous solutions used as electrolytes and the discharge potentials are higher than those of the non-aqueous systems, namely in the range 3.0–3.3 V depending on the solution pH. As previously discussed, the key problem is the protection of Li anode. The typical aqueous solution is the mixture LiOH–LiCl–H$_2$O [58,69], in which the LiCl concentration and/or pH can vary [102]. Such parameters, and in particular the solution acidity, affect the LiOH amount in the discharge step. However, many other systems were considered, such as diluted LiOH, chloric acid/LiClO$_4$, HNO$_3$/LiNO$_3$ etc. [103].

The most recent advances concern with the development of hybrid configurations, in which the Li anode in non-aqueous electrolyte and the air catalytic cathode in an aqueous electrolyte are separated by a ceramic LISICON or NASICON film [104]. In such dual-electrolyte rechargeable Li/air cells, the aqueous compartment may also be constituted by acetic acid (90 vol%)–H$_2$O–Li acetate salt (10 vol%), 1.0 M KOH, or also phosphate buffer catholyte like 0.1 M H$_3$PO$_4$/1.0 M LiH$_2$PO$_4$. In the latter case, for instance, the solid electrolyte separates the aprotic solvents from the aqueous solution, and provides paths for Li$^+$ transport. In particular, the buffer solution with low pH guarantees the solid electrolyte stability, reducing the internal resistance and providing high working voltage and energy density. Discharge capacity of
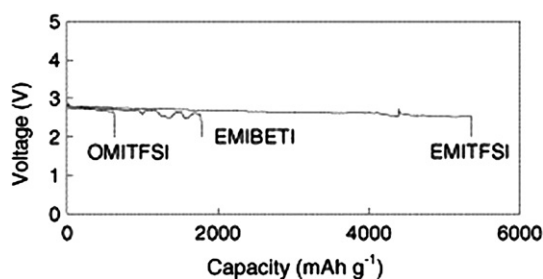

Fig. 13. Discharge profiles of ionic liquid-based Li–air cells at 20 °C in air and at 0.01 mA cm^{-2} (taken from Ref. [95] with permission from Elsevier).

221 mAh g^{-1} with good cycling behaviour was observed at a current density of 0.5 mA cm^{-2} [105].

5. Future developments

At present, the Technology Readiness Level [106] of rechargeable LABs is between 3 and 4, which means "Research to Prove Feasibility/Technology Development" [107]. A reasonable estimation of the time-to-market may be around 10–15 years for portable electronics applications, in a similar manner to what happened for the first Sony's LiCoO$_2$ based battery. Concerning the more demanding requests for automotive, even longer times of the order of 35 years could be envisaged [73]. Indeed, to make LABs a commercial product many research studies are needed because, as we discussed above, the different battery components still present many unresolved issues. A key point is the development of a carbon cathode with an optimal mesoporous structure, and a membrane to prevent the CO$_2$ and moisture migration into the air-electrode while allowing O$_2$ diffusion and mass transport. Further investigations are required to understand the real role played by the catalyst in the charge/discharge processes. A stable lithium metal anode able to sustain numerous cycling has still to be built up, and some efforts have to be done to solve the safety issues.

Another key point is the development of more performing electrolytes and the optimization of the interfaces. In the case of aqueous batteries, a water-stable electrode is mandatory and the ceramic layer used for the anode protection needs further optimization in terms of conductivity and improvement of the interface contacts. In turn, the electrolyte should assure a sufficient O$_2$ and discharge products solubility. A proper system to adjust water consumption/production for alkaline or acidic media may be also needed during long term operation. For non-aqueous systems the discovery and optimization of new electrolyte families is fundamental to obtain high power densities and good rechargeability. An overall improvement of the LABs performance is also requested to pursuit higher current densities, which are mandatory for most commercial applications (e.g. in automotive). Notwithstanding the numerous and serious problems which remain to be solved, lithium air batteries are very interesting because of their potential high energy density, and likely deserve the strong R&D efforts at present undertaken by both industrial and academic labs.

Acknowledgements

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